

# Copolymers for Water Base Paints

## From Vinyl Acetate

## And Long-Chain Vinyl Esters

839

By WILLIAM S. PORT, FRED A. KINCL\* and DANIEL SWERN†

United States Department of Agriculture

Water base paints have been known for many years, but it was not until the end of World War II that they were extensively used. The particular stimuli which possibly led to the expansion of the latex paint industry in this country were the knowledge obtained during the war in making stable synthetic rubber emulsions and the establishment of the synthetic rubber industry which made available a constant latex supply at a low price. Another possible factor was the boom in housing developments with the attendant large growth in decoration by the small-home owners themselves, who were unwilling to pay for the labor cost in painting and who, being unskilled, demanded a paint that could be applied easily and with a minimum of preparation.

Whereas in the United States the already existing huge synthetic rubber industry led to latex paints having a binder film of a butadiene-styrene copolymer, in Europe, because of the short supply of petroleum (a source of GR-S intermediates), other polymers, especially polyvinyl acetate, were favored. Because polyvinyl acetate emulsion paints have certain intrinsic advantages, interest in them has developed recently in this country. They are now being offered commercially in the United States, and it is anticipated that the new industry will grow enormously within the next few years.

Some of the advantages offered by polyvinyl acetate emulsion paints are high gloss, strong adhesion to many surfaces, and non-yellowing characteristics. Among the problems introduced by the use of polyvinyl acetate as a binder film, on the other hand, are water-sensitivity<sup>1</sup> and the necessity for the addition of external plasticizers.

One way in which water-sensitivity is manifested is the appearance of a whitened surface within seconds when a drop of water is placed on a polyvinyl acetate film cast from an emulsion. When the water is removed by careful blotting, a white spot remains. More vigorous removal of the water by wiping deeply abrades the film and even results in film failure. The seriousness of this problem both in ultimate film life and in immediate effect on dark colors is obvious. The causes of water sensitivity are complex, depending not only upon polymer type but also on each of the many different components in a paint film. The proper choice of emulsifiers, thickening agents, and protective colloids is probably of primary importance in mitigating water sensitivity because these substances are of necessity hydrophilic. An alternative approach which seems reasonable

\* Fellow of the National Renderers' Association.

† Agricultural Research Service, Eastern Utilization Research Branch, Philadelphia 18, Pa.

is modification of the base polyvinyl acetate film to promote water repellency.

Plasticization is necessary in order to lower the temperature at which a continuous polymer film will form. Since the brittle temperature (more precisely, the second-order transition temperature) of polyvinyl acetate is about 85°F., which is higher than the temperature usually encountered during painting, some means must be provided for lowering the flow temperature. Although the technical difficulties in adding an external plasticizer to a polyvinyl acetate latex can be satisfactorily overcome, such a procedure has several drawbacks. First, an additional operation is added to the manufacturing process with attendant increase in costs due to time and labor.

A second and more important drawback is the loss of plasticizer which may occur in an externally plasticized film. Although an external plasticizer usually boils at a high temperature, serious loss of plasticizer by evaporation will occur in a short time, relative to the required life of the film, because paint is applied as a thin coating with a consequent high surface to volume ratio. Loss of external plasticizer may also occur by migration into an adjoining surface. The extent of the loss will depend, in part, on the porosity of the surface and the migration characteristics of the plasticizer. The mobility of the plasticizer also brings it to the outer surface of the film as a thin coat where it is removed by washing during rains and wiping in household cleaning. The repeated process of washing and remigration will, in time, seriously reduce the concentration of plasticizer. Both migration and volatilization, therefore, give rise to a film of constantly changing properties and ultimately produce a film so low in plasticizer content, that it is brittle and is subject to mechanical shock failure. Loss of plasticizer is undesirable for the additional reason that any secondary advantages that a plasticizer may bring, such as decreased water sensitivity, are lost. Volatilization of a plasticizer is undesirable indoors because of possible odor problems.

A third drawback to the use of external plasticizers is incompatibility or limited compatibility of plasticizers whose price and chemical properties would make them otherwise desirable. For example, esters of long-chain fatty acids are low in price and should impart water repellency but cannot be used with polyvinyl acetate because of incompatibility.

A promising approach to the problem of lowering the second-order transition temperature and one which also avoids the problems of volatilization and migration of plasticizer is structural modification of polyvinyl acetate by copolymerization. Since the "plasticizing" comonomer is an integral part of the copolymer, it cannot evaporate or migrate. In contrast with external modification, plasticization by copolymerization avoids completely the problem of incompatibility since all reasonably homogeneous copolymers are compatible. Furthermore, to a certain extent there is an increase in the range of types of chemical structures which may be built into the copolymers with their attendant effects on the physical properties of these copolymers, notably increased water resistance. However, limitations are imposed in the choice of comonomer because some monomer pairs either will not copolymerize or they give rise to a mixture of copolymers of wide compositional heterogeneity. Copolymer compositional heterogeneity may be the cause of incompatibility or of reduced strength and gloss.

An index to good copolymerizability is found in a set of constants for each monomer pair called the monomer reactivity ratios,  $r_1$  and  $r_2$ .<sup>2,3</sup> To obtain a copolymer of high compositional homogeneity throughout the whole range of comonomer compositions, it is necessary that  $r_1$  and  $r_2$  both approximate unity. This fortuitous situation exists with vinyl acetate and long-chain vinyl esters.

This paper describes the preparation of water emulsions of internally (or structurally) plasticized copolymers of vinyl acetate with long-chain vinyl esters. The particular long-chain vinyl esters which are useful for this purpose are vinyl stearate, vinyl palmitate, and their mixtures. A raw material source for these vinyl esters is the large surplus of inedible animal fats which are produced in this country at an annual rate of more than two billion pounds at a selling price of about 5-8 cents per pound. A steady, large and low-cost raw material supply is therefore ensured. Briefly, one synthesis of the vinyl esters consists of treating the fatty acid with acetylene under moderate pressure at about 160°C. in the presence of a zinc catalyst and separating the catalyst for subsequent reuse.<sup>4</sup> Thus, because of the low price of raw materials and the simplicity of the process, a low price can be expected for the monomer. Although the long-chain vinyl esters are not yet available commercially, several manufacturers offer them on a pilot plant scale. These companies have estimated that the price of the monomers should be in the order of 50-60 cents per pound and, if the market should develop according to expectations, the price should be about 30-40 cents per pound. One may expect, therefore, that the price of long-chain vinyl esters will be sufficiently attractive to warrant examination of their chemical behavior and use in various applications.

Previous work<sup>5</sup> on the chemistry of vinyl palmitate or vinyl stearate has shown that in copolymerization with vinyl acetate, the long chain vinyl ester enters into the copolymer at nearly the same rate as does vinyl acetate. Specifically, the monomer reactivity ratios for the system vinyl acetate-vinyl palmitate are 1.15 and 0.78. This chemical property of the long chain vinyl esters is valuable because mixtures of all proportions of vinyl acetate and vinyl stearate (or vinyl palmitate) will react to form copolymers having nearly the same composition as the monomer mixture at any conversion. This is not true of all pairs of monomers. For example,<sup>6</sup> when vinyl acetate ( $M_1$ ) and an acrylic ester ( $M_2$ ) react, the acrylic ester enters into the copolymer more rapidly than does vinyl acetate ( $r_1 = 0.1$ ,  $r_2 = 9$ ). As the reaction proceeds, the supply of the acrylic ester is depleted and the composition of the resulting copolymer changes with conversion.

The preparation of copolymers of vinyl acetate and long-chain vinyl esters is technologically simple. A recipe is given in *Table 1*. Vinyl palmitate or mixtures of vinyl palmitate and vinyl stearate may be substituted for vinyl stearate and the amount of the long-chain vinyl ester may be increased to about 35%, if desired. Other emulsifiers and other initiators probably may be used, but we have not investigated them extensively.

To obtain a latex free from coagulum, it is important to obtain a good emulsion of the long-chain vinyl ester before beginning polymerization. This is accomplished by melting the vinyl stearate (m.p. 95°F.) and adding the emulsifier with efficient mechanical agitation and slowly adding the water. In this laboratory, for example, a high speed blender is used. Alternatively, a solution of the emulsifier may be added to the

**Table 1—Recipe for the Preparation of a Latex of Polyvinyl Acetate-Stearate**

Vinyl Acetate	81.6 parts
Vinyl Stearate	15.4
Water	97.0
Sulfonated Red Oil (100% basis)*	4.0
Potassium Persulfate	0.54

Melt the vinyl stearate, add the sulfonated red oil and, with vigorous mechanical stirring, add, in sequence, the water, the vinyl acetate and the potassium persulfate. Raise the temperature to 120°F. and heat for four hours, gradually raising the temperature to 160°F. Blow out any traces of vinyl acetate with steam.

\* Two parts each of Triton W31 and Span 20 (on 100% basis) may be substituted for the sulfonated red oil. Reference to commercial products in this report is not intended to be a recommendation of these products by the United States Department of Agriculture over others not mentioned.

rapidly stirred long-chain vinyl ester. The emulsion is then transferred to a polymerization flask, the initiator and the vinyl acetate are added and the emulsion is heated to 120°F. As the polymerization reaction proceeds, the temperature is gradually raised to 160°F. for a total heating time of four hours. Traces of vinyl acetate are then removed by passing steam through the emulsion.

Tough, strongly-adhering, permanently flexible films can be cast from these emulsions. They show good water resistance; in the spotting test, whitening occurs only after five minutes. On removal of the water the discoloration disappears rapidly and the film, when rubbed, is abraded only at the surface. The second order transition temperature, as measured by the brittle temperature,<sup>7</sup> is lowered as the long-chain vinyl ester content is increased (Table 2).

In summary, it may be said that copolymers of vinyl acetate and vinyl stearate (or vinyl palmitate) offer advantages to the paint industry because they are internally (structurally) plasticized and, therefore, show good film fusion at temperatures ordinarily met in painting. They are inexpensive, compositionally homogeneous, and they show increased water resistance. In addition, they do not manifest the disadvantages of migration and volatility shown by externally plasticized compositions. It is obvious that much work remains to be done before suitable water-emulsion paints may be made from copolymers of vinyl acetate and vinyl stearate. Such information as the mode of addition and the effect of thickening agents, protective colloids and pigments must be studied. It is hoped, however, that information on the preparation of suitable latexes

**Table 2—Brittle Temperatures of Copolymers of Vinyl Acetate And Vinyl Esters of Long-Chain Fatty Acids**

Vinyl Acetate-Palmitate Copolymers		Vinyl Acetate-Stearate Copolymers	
Vinyl Palmitate Weight %	Brittle Temperature °F.	Vinyl Stearate Weight %	Brittle Temperature °F.
0	88	0	88
15	72	14	73
25	54	26	54
33	48	36	52

of polyvinyl acetate-stearate will be of help in starting further investigative work by paint formulators.

#### REFERENCES

- (1) H. Naidus, *Ind. Eng. Chem.* 45, 715 (1953).
- (2) T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.* 12, 205 (1944).
- (3) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.* 66, 1594 (1944).
- (4) Paper to be presented at the Spring 1954 meeting of the American Chemical Society by L. E. Craig, R. W. Davis, R. F. Kleinschmidt, E. S. Miller, C. F. Montross, and W. S. Port.
- (5) W. S. Port, E. F. Jordan, Jr., J. E. Hansen, and D. Swern, *J. Polymer Sci.* 9, 493-502 (1952).
- (6) F. R. Mayo, F. M. Lewis and C. Walling, *J. Am. Chem. Soc.* 70, 1529 (1948).
- (7) M. L. Selker, G. G. Winspear and A. R. Kemp, *Ind. Eng. Chem.* 34, 157 (1942).